Synthesis and Properties of Photochromic Fluorescing 2-Indolyl Fulgide and Fulgimide Copolymers

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ABSTRACT: We have designed and synthesized new, novel photochromic copolymers composed of photochromic 2-indolyl fulgides or fulgimides and methyl methacrylate. The spectroscopic and photochromic properties of these copolymers have been determined and compared to their liquid solution analogues. The utilization and advantages of these materials for use in optical switching and optical storage devices are discussed.

Introduction

In previous papers we have described the photochromic and spectroscopic properties of several new photochromic 2-indolyl fulgides and fulgimides.[1−4] These molecules exhibit thermally irreversible photochromic reactions, and in addition the cyclized forms emit fluorescence. These unique properties make them potentially useful for applications in optical storage devices and optical switching.[5−10] All data, presented and discussed in previous publications, were obtained in liquid solutions. However, technological devices demand, almost always, that the photochromic materials be in the condensed phase and at high concentrations. For example, photochromic materials used in 3D optical memory devices, based on two-photon absorption, require concentrations of 10^{-1} M and higher in order for the device to perform at the required writing and reading efficiencies.[5] Should it be possible to form copolymers that contain the photochromic functional groups, the concentration of the photochromic materials would vastly increase.[11,12] In addition to the high concentration of the photochrome, copolymers also have the following advantages: (1) the photochromphores are distributed uniformly, (2) the aggregates that are usually formed in liquid mixtures are not observed in the copolymer, and (3) the photochromic molecules do not diffuse through the matrix.

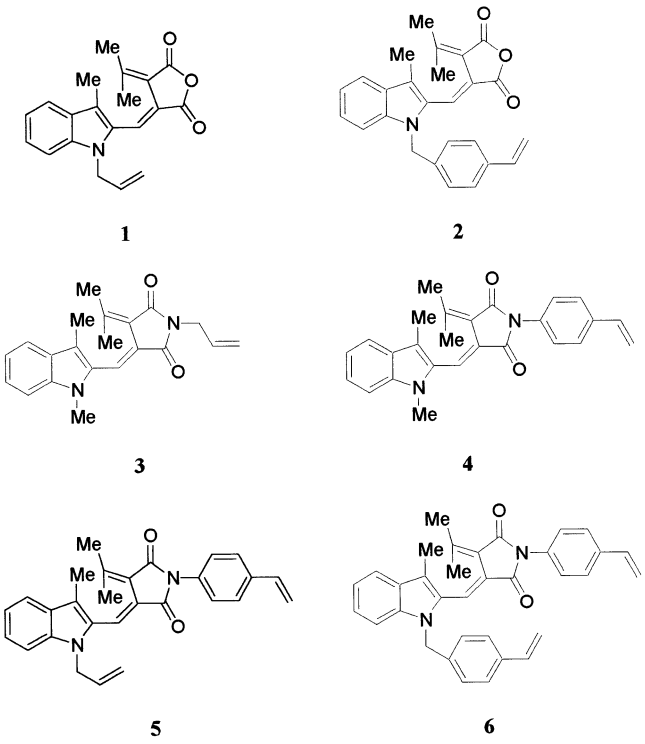
In this paper we describe the synthesis and properties of several new fluorescing photochromic 2-indolyl fulgides and fulgimides, which have been copolymerized with methyl methacrylate (MMA). It is also very possible to copolymerize these photochromic molecules with several other monomers to form new photochromic copolymers with distinct properties. We have compared and present the photochromic and spectroscopic properties of 2-indolyl fulgides and fulgimides dispersed in poly(methyl methacrylate) (PMMA) matrices with these of the copolymers.

Results and Discussion

Photochromic Molecules Capable of Copolymerization with MMA. A number of fulgides and fulgimides containing styrene or propylene groups were designed, synthesized, and used for the synthesis of photochromic copolymers (see Scheme 1).

Fulgides **1** and **2** were synthesized by the procedure shown in Scheme 2. Commercially available 3-methylindole (**7**) was converted to **8** by reaction with allyl bromide or to **9** by reaction with 4-vinylbenzyl chloride, in potassium hydroxide−DMSO solution.[13] Products **8** and **9** were then converted to their corresponding products **10** and **11** using the Vilsmeier−Haack formylation reaction.[14] Stobbe condensation of indole-2-carboxaldehyde (**10**, **11**) with diethylisopropylidene succinate (**12**) followed by hydrolysis and intramolecular acid anhydride formation yields 2-indolyl fulgides **1** and **2**.[15,16]

Scheme 1



The synthesis of fulgimides **3** and **4** has been described in ref 2. Fulgimides **5** and **6** were prepared by the same method (see Scheme 3).

Photochromic Copolymers of Fulgides and Fulgimides with PMMA. To prepare copolymers of PMMA with photochromic fulgides **1**, **2** and fulgimides **3**−**6**, the corresponding solutions of photochromes in MMA were polymerized by radical polymerization in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) initiator. The polymerization of these solutions, sealed under vacuum

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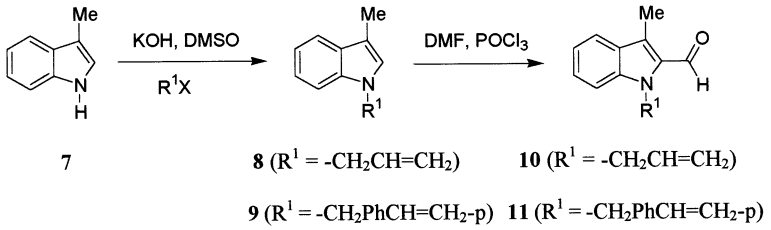
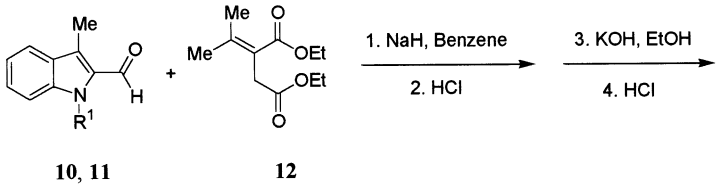
Scheme 2

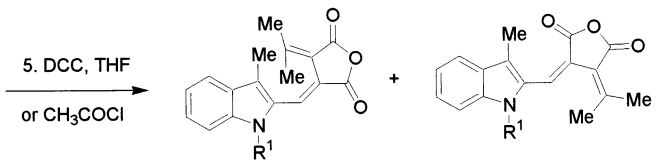


7 **8** (R^1 = -$CH_2CH{=}CH_2$) **10** (R^1 = -$CH_2CH{=}CH_2$)

9 (R^1 = -$CH_2PhCH{=}CH_2$-p) **11** (R^1 = -$CH_2PhCH{=}CH_2$-p)



10, 11 **12**

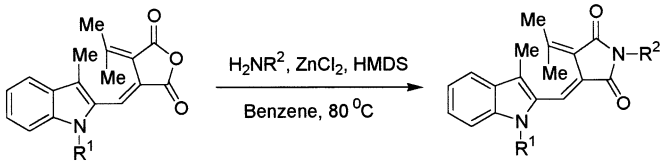


E ***Z***

1 (R^1 = -$CH_2CH{=}CH_2$)

2 (R^1 = -$CH_2PhCH{=}CH_2$-p)

Scheme 3



R^2 = -$C_6H_4CH{=}CH_2$(p)

1 (R^1 = -$CH_2CH{=}CH_2$) **5** (R^1 = -$CH_2CH{=}CH_2$)

2 (R^1 = -$CH_2PhCH{=}CH_2$-p) **6** (R^1 = -$CH_2PhCH{=}CH_2$-p)

in glass cells, was carried out at 50 °C for 24 h. A lower concentration of 1×10^{-4} mol/L was used for photochemical studies, and higher concentration such as 1×10^{-2} mol/L was employed to investigate the polymerization reaction. These resulted in the uniform rigid and optically clear polymers depicted in Scheme 4. During polymerization, except for a trace of cyclized form that was formed, which was evidenced by reverting back to its open form when irradiated with visible light, no any other side reaction was observed. The T_g of the copolymers, excluding cross-linked polymer, was found to be 112 °C and the number-average molecular mass for copolymer **4** to be 784 000.

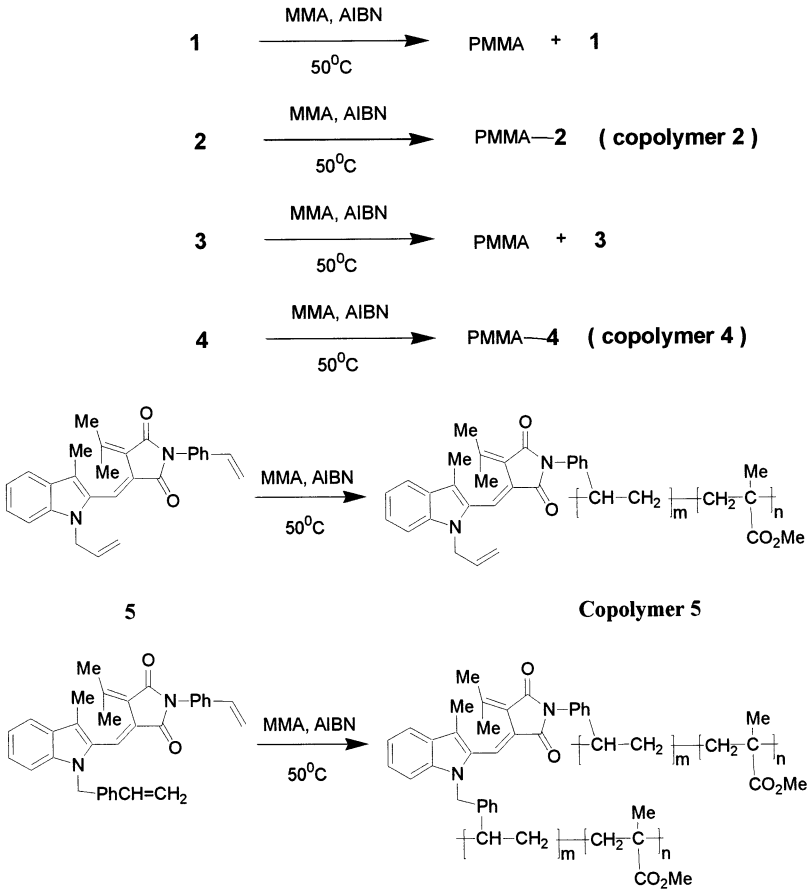
These photochromic copolymers were found to have very good thermal stability at room temperature.

To evaluate the affinity of the photochromic fulgides and fulgimides **1**−**6** to form copolymers with PMMA, we dissolve the copolymer, described above, in 1,2-dichloroethane, where both PMMA and the photochromic molecules are very soluble. Subsequently, hexane solvent was added to precipitate the polymer. The percipitate was separated from the solution, and both the precipitated polymer and the diluted solution were analyzed for the presence of photochromic molecules. The solutions containing the polymers derived from fulgide **2**, fulgimide **4**, and **5** formed yellow solid polymer precipitates. The absorption spectra of these precipitates showed the characteristic chromophore spectra; in contrast, the solutions did not show any traces of fulgide **2**, fulgimide **4**, and **5**. These data prove uniequivocally that the photochromic molecules **2**, **4**, and **5** were chemically bonded to the polymer chain of the PMMA forming a copolymer.

In the case of fulgide **1** and fulgimide **3** polymerization, the opposite was observed. The photochromic fulgide **1** and fulgimide **3** were found in the solutions, while the precipitated polymer was found to contain only pure PMMA.

In contrast, fulgimide **6**, onto which are attached two styrene groups capable of reacting with MMA, we found

Scheme 4



that this photochromic molecule, after polymerization, was an integral part of the polymer product and did not remain in solution. However, unlike the other copolymers that we have created, the copolymer of fulgimide **6** and PMMA is not soluble in 1,2-dichchloroethane but forms only a gel. This indicates that it has a cross-linked structure because both styrene groups take part in the polymerization reaction, and the fulgimide moiety bridges two polymer chains, forming an insoluble 3D cross-linked structure. This cross-linked structure is shown in Scheme 4.

Photochromic Properties of Copolymers. All copolymers of fulgides and fulgimides with PMMA described above were found to be photochromic; i.e., they can be reversibly colored (cyclized) and bleached (open) by irradiation with light of the appropriate wavelength. The mechanism of the photochromic reaction that induces structural changes in fulgide or fulgimide moieties is based on the reversible light-induced hexatriene (open-ring, *E*-form)/cyclohexadiene (cyclized, *C*-form) interconversion, shown in Scheme 5. In addition, the cyclized forms of the copolymers emit fluorescence when excited with visible light, as is the case with photochromes, alone in solution. Figure 1 shows the absorption spectra of the cross-linked copolymer **6** in its *E*-form and *C*-forms and the fluorescence spectrum of the *C*-form. The *C*-form was photoinduced by irradiating the copolymer with 400 nm light. When the *C*-form was irradiated with visible light, $\lambda = 530$ nm, it easily bleached back to the original *E*-form.

The maxima of the absorption spectra bands of the open-ring (*E*) and cyclized (*C*) forms of the copolymers

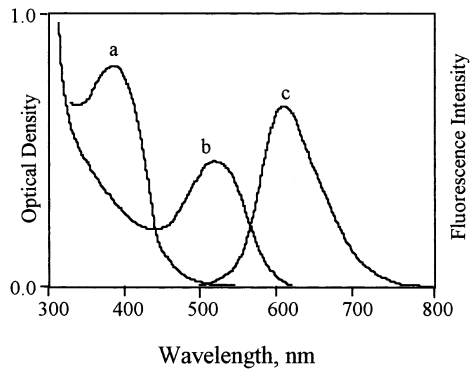
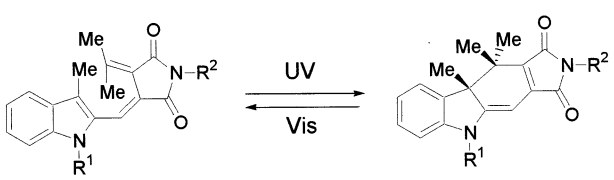


Figure 1. Absorption and fluorescence spectra of cross-linked copolymer **6**: (a) absorption spectrum of the *E*-form; (b) and (c) absorption and fluorescence spectra of the *C*-form, respectively.

Scheme 5



and their quantum yields for coloration and bleaching photoreactions are listed in Table 1. Because the polarity of PMMA is close to that of ethyl acetate, the absorption spectra maxima and photoreaction quantum

Table 1. Absorption Spectra Maxima and Photoreaction Quantum Yields of 2, 4, and 6 and Their PMMA Copolymers

	λ_{max}, nm (ϵ), *E* form		Φ_{E-C}		λ_{max}, nm (ϵ), *C* form		Φ_{C-E}	
	copolymer	EtOAC	copolymer	EtOAC	copolymer	EtOAC	copolymer	EtOAC
2	396	394 (13800)	0.13	0.12	502	500 (13800)	0.21	0.20
4	388	387 (15500)	0.14	0.12	518	517 (11000)	0.17	0.11
6	387	382 (16300)	0.13	0.12	518	513 (10900)	0.17	0.10

Table 2. Fluorescence Emission Spectra Maxima and Fluorescence Quantum Yields of 2, 4, and 6 and Their PMMA Copolymers

	EtOAc		copolymer	
	λ_{max}, nm	Φ_{Fl}	λ_{max}, nm	Φ_{Fl}
2	585	0.04	582	0.13
4	621	0.04	612	0.04
6	616	0.03	610	0.05

yields of **2, 4**, and **6** in ethyl acetate solution are also listed for comparison. Our data show that the photochromic copolymers of **2**, **4**, and **6** exhibit the same photochromic reaction efficiencies as the photochromic materials in ethyl acetate solutions.

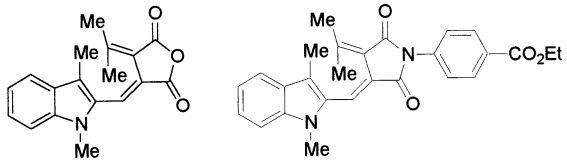
We might expect that the rigid photochromic copolymers, especially the cross-linked copolymers where both ends of the fulgimide moiety are attached to polymer chains, will exhibit a higher quantum yield for the coloration reaction, owing to the possible reduction in the rate of the competing *E*−*Z* isomerization. However, the data presented in Table 1 show that the quantum yields for the coloration and bleaching photoreactions for copolymers **2**, **4**, and **6** are the same as the ones measured in pure **2, 4**, and **6** in ethyl acetate solutions. This indicates that the solid matrix does not decrease the *E*−*Z* isomerization rate, but rather, it remains the same in both the copolymers and solution.

We have also investigated the fatigue resitance of the obtained copolymers by measuring the photochromic ring-closing/ring-opening (coloration/bleaching) cycles. After 100 photochromic cycles there are still more than 90% of the photochrome remains photochromic based on the concentration of the cyclized form which absobs at longer wavelength and does not overlap with the assumed decomposed products.

The *C*-forms of the fulgides and fulgimides PMMA copolymers emit red fluorescence under 530 nm light excitation. The maxima of the fluorescence spectra and the fluorescence quantum yields for copolymers **2, 4**, and **6,** as well as pure **2, 4**, and **6** in ethyl acetate solutions, are listed in Table 2.

To ensure that we have indeed synthesized a true photochromic copolymer whose *C*-form group fluoresces, it was mandatory to prove that the fluorescence is emitted by the cyclized form of the photochrome groups of the copolymer rather than impurities or other species. To this effect the excitation and fluorescence spectra were measured during bleaching/coloration cycles. We established that the fluorescence excitation spectra corresponded to the absorption spectra of the colored forms. It was also observed that the intensity of the fluorescence and fluorescence excitation spectra decreased proportionally with the decrease in the cyclized form optical density, i.e., concentration, when the *C*-form is transferred to the *E*-form by light. When the materials were completely bleached, depicted when the absorption band of the *C*-forms has completely disappeared, no fluorescence was detected. During the coloration cycle, the fluorescence appeared again and increased with the same rate as the rate of growth of the *C*-form absorption. These data unequivocally confirm that the fluorescence is emitted by the cyclized *C*-forms.

Scheme 6



13 **14**

Photochromic Molecules Directly Dispersed in PMMA. The photochromic properties of fulgide **13** and fulgimide **14**, shown in Scheme 6, were measured while dispersed in PMMA matrices and in solutions that are used as reference. The synthesis of these molecules has been described elsewhere.[4]

The homogeneous PMMA/fulgide **13** or fulgimide **14** samples were prepared by radical polymerization of MMA monomer solutions initiated by AIBN polymerization initiator. The homogeneous bulk PMMA/chromophore samples were cut and polished to optical quality and used to perform spectroscopic and 3D optical storage studies.

Table 3 shows the absorption spectra maxima and photoreaction quantum yields of fulgide **13** and fulgimide **14** in ethyl acetate solution and in PMMA matrixes, respectively. The ethyl acetate solutions were also used to compare the photochromic properties of the liquid solutions with the solid polymer matrices. Their fluorescence emission maxima and fluorescence quantum yields are listed in Table 4.

The data show that fulgide **13** and fulgimide **14** dispersed in solid PMMA matrices and dissolved in ethyl acetate have the same photochromic reaction efficiencies and are not affected by the degree of hardness of the polymer host. However, the fluorescence quantum efficiencies are significantly higher in PMMA compared to liquid solutions. This is probably due to the decrease in the efficiency of the radiationless processes that are competing with fluorescence in the rigid polymer matrix.

Experimental Section

General. Fulgides **1** and **2** were obtained directly by Stobbe condensation of the corresponding **10** and **11** with diethylisopropylidene succinate. Fulgimides **3**−**6** were transformed directly from the corresponding fulgides by Lewis acid and hexamethyldisilazane (HMDS) promoted reaction. The crude products were purified by column chromatography and subsequent recrystallization. The cyclized forms (*C*-form) of each fulgide or fulgimide were prepared by irradiating the *E*-form fulgide or fulgimides in acetonitrile solution with 390−400 nm light and subsequent removal of the solvent under reduced pressure. The *C*-form of each fulgide or fulgimide copolymer was also prepared by irradiating the *E*-form fulgide or fulgimides copolymers with 390−400 nm light. The structure and purity of the synthesized compounds were ascertained by NMR, MS, and elemental analysis. All solvents were HPLC grade or spectral grade and were used without further purification. All spectra and quantum yields in solution were measured in 1 cm quartz cells at room temperature. The UV−

Table 3. Absorption Spectra Maxima and Photoreaction Quantum Yields of Fulgide 13 and Fulgimide 14 Dissolved in Ethyl Acetate and Dispersed in PMMA Polymer Matrix

	λ_{max}, nm (ϵ), *E* form		Φ_{E-C}		λ_{max}, nm (ϵ), *C* form		Φ_{C-E}	
	EtOAC	PMMA	EtOAC	PMMA	EtOAC	PMMA	EtOAC	PMMA
13	394 (12700)	398	0.14	0.15	502 (13000)	505	0.21	0.21
14	388 (13500)	390	0.14	0.15	520 (10200)	525	0.13	0.14

Table 4. Fluorescence Emission Spectra Maxima and Fluorescence Quantum Yields of Fulgide 13 and Fulgimide 14 Colored Form Dissolved in Ethyl Acetate and Dispersed in PMMA Bulk Polymer Matrix

	EtOAc		PMMA	
	λ_{max}, nm (*E* form)	Φ_{Fl}[a]	λ_{max}, nm (*C* form)	Φ_{Fl}[a]
13	590	0.05	586	0.15
14	620	0.05	615	0.11

[a] $\lambda_{ex} = 550$ nm.

vis absorption and fluorescence spectra were recorded by means of a Shimadzu UV 160 spectrophotometer and a Shimadzu RF 5000U spectrofluorophotometer, respectively. ^{1}H NMR spectra were obtained by means of a DRX-400 (400 MHz) or a GN 500 (500 MHz) NMR spectrometer (tetramethylsilane the internal standard). MS spectra were obtained using a VG Analytical 7070E mass spectrometer.

Photoexcitation was carried out using a 150 W xenon arc lamp (Oriel). Light of the appropriate wavelength was selected by either a monochromator or cutoff optical filters (Hoya). The quantum yields of the photochromic reaction, ring-closure (coloration) and ring-opening (bleaching) in solution or in polymer were determined by comparison with the photochromic reaction yield of (*E*)-(**13**) in acetonitrile. Fluorescence quantum yields of the samples were measured relative to fulgide **13,** as described in ref 3.

Synthesis: **2-[1-Allyl-3-methyl-2-indolylmethylene]-3-isopropylidenesuccinic Anhydride** (**1**). To a flask charged with sodium hydride (95%, 4.3 g, 170 mmol) and 80 mL of anhydrous benzene, a mixture of **10** (15.95 g, 80 mmol) and **12** (17.15 g, 80 mmol) in anhydrous benzene was added dropwise at room temperature. After 1 mL of the above mixture were added, 2 drops of ethanol was added to initiate the reaction, followed by the addition of the remainder in a period of 3 h. When the addition was complete, the reaction was stirred at room temperature for 16 h. The reaction was subsequently quenched with ethanol, and the mixture was poured onto crushed ice (200 g). The organic layer was separated and extracted with two 100 mL portions of aqueous sodium hydroxide (2 M). All the aqueous layers were combined and acidified with hydrochloric acid (5 M). The liberated half ester was extracted with ethyl acetate (3 × 150 mL). After the evaporation of the solvent and purification by silica gel column chromatograph, the half ester was collected as a yellow powder (24 g, 82%).

This half ester was hydrolyzed in potassium hydroxide−ethanol solution (24 g/300 mL) under reflux for 6 h. When the flask was cooled to room temperature, the resulting dipotassium salt was filtered and washed with ethanol. The dipotassium salt was then dissolved in water (150 mL) and acidified with hydrochloric acid. Crude diacid was obtained after filtration with suction and washing with water. Yellow crystals (14.1 g, 64%) were afforded by passing the crude product to a silica gel chromatography column (eluted with chloroform−ethyl acetate) and recrystallization from chloroform−hexane three times.

To a flask charged with dried diacid (10.2 g, 30 mmol) and anhydrous THF (200 mL), dicyclohexylcarbodiimide (DCC) (6.4 g, 31 mmol) was added. The mixture was stirred at room temperature in dark for 3 h. Then the resulting mixture was filtered. The filtrate was condensed by rotary evaporation. Yellow crystals (8.6 g, 89%) were afforded by passing the crude product through the silica gel column chromatography (eluted with chloroform−ethyl acetate) and recrystallization from ethanol and hexane−chloroform. **1**: mp 125−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.32 (s, 3H), 1.86 (s, 3H), 2.54 (s, 3H), 4.79 (m, 2H), 4.93 (dd, J = 17.6, 0.8 Hz, H), 5.17 (dd, J = 10.4, 0.8 Hz, H), 5.87−5.91 (m, H), 7.14−7.32 (m, 3H), 7.62 (d, J = 8 Hz, H), 7.74 (s, H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 11.2, 23.4, 27.6, 46.3, 109.6, 117.3, 117.7, 120.0, 120.1, 120.3, 122.6, 124.7, 125.0, 127.4, 131.7, 132.5, 138.4, 159.3, 163.0, 165.6. HRMS (CI): Calcd for $C_{20}H_{19}NO_3$, *m*/*z* 321.1365. Found: 321.1368. Anal. Calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.62; H, 6.02; N, 4.33.

2-[3-Methyl-1-(4-vinylbenzyl)-2-indolylmethylene]-3-isopropylidenesuccinic Anhydride (**2**)**.** The same set as above; to a flask with sodium hydride (95%, 1.7 g, 67 mmol) and 100 mL of anhydrous benzene, a mixture of **11** (8.8 g, 32 mmol) and **12** (7.2 g, 33 mmol) in anhydrous benzene was added dropwise to the flask. The reaction was quenched with ethanol, and the mixture was poured onto crushed ice (200 g) and acidified with hydrochloric acid. The resulting half ester was extracted with ethyl acetate (4 × 150 mL). After the evaporation of the solvent and purification by silica gel column chromatograph, the half ester was collected as oil (10.7 g, 75%). This half ester was hydrolyzed in potassium hydroxide−ethanol solution (24 g/300 mL) under reflux for 6 h. The resulting dipotassium salt was filtered and washed with ethanol. The dipotassium salt was then dissolved in water (150 mL) and acidified with hydrochloric acid. Crude diacid was obtained after filtration with suction and washing with water. Diacids (5.6 g) were afforded by passing the crude product through the silica gel column chromatography (eluted with chloroform−ethyl acetate).

To a flask with dried diacid (1.25 g, 3 mmol) and anhydrous THF (40 mL), DCC (0.7 g, 3.4 mmol) was added. The mixture was stirred at room temperature in dark for 3 h. The resulting mixture was filtered with suction. The filtrate was condensed by evaporation. Yellow crystals (0.43 g, 36%) were afforded after purification by means of silica gel column chromatography (eluted with chloroform−ethyl acetate) and recrystallization from ethanol diethyl ether. **2**: mp 147.5−149 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.12 (s, 3H), 1.86 (s, 3H), 2.49 (s, 3H), 5.22 (dd, J = 10.9, 0.6 Hz, H), 5.34 (d, J = 17.6 Hz, H), 5.41 (d, J = 17.6), 5.68 (dd, J = 17.6, 0.7 Hz, H), 6.62 (dd, J = 17.6, 10.9 Hz, H), 6.99 (d, J = 8.2 Hz, 1H), 7.18−7.34 (m, 5H), 7.64 (d, J = 8 Hz, H), 7.73 (s, H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 11.6, 23.7, 27.7, 47.7, 111.0, 114.6, 118.4, 120.3, 120.6, 122.8, 125.3, 125.3, 126.9, 126.9.4, 127.0, 132.1, 136.4, 136.7, 137.6, 139.1, 159.8, 163.2, 165.8. HRMS (CI): Calcd for $C_{26}H_{23}NO_3$, *m*/*z* 397.1678. Found: 397.1676. Anal. Calcd for $C_{26}H_{23}NO_3$: C, 78.57; H, 5.83; N, 3.52. Found: C, 78.62; H, 5.79; N, 3.53.

2-[1-Allyl-3-methyl-2-indolylmethene]-3-isopropylidene-*N*-(4-vinylphenyl)succinimide (**5**) A flask is charged with a solution of fulgide **1** (0.301 g, 0.94 mmol) in benzene (15 mL). Through a dropping funnel, 4-vinylaniline (90%, 0.12 mL, 0.94 mmol) in benzene (5 mL) was added dropwise, and the reaction mixture was stirred for 1 h at room temperature. To this reaction mixture, zinc chloride powder (0.94 mmol) was added in one portion. Subsequently, the reaction mixture was heated to refluxing temperature (80 °C), followed by the addition of hexamethyldisilazane (0.30 mL, 1.4 mmol) in benzene (5 mL), through dropping funnel, over a period of 10 min. This reaction mixture was then refluxed for 20 h. The benzene solvent was removed by rotary evaporation. The crude product was purified by means of flash silica gel chromatography column (chloroform as eluent) to afford a bright yellow crystal **5** (0.188 g, 47%). **5**: mp 171.5−172.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.34 (s, 3H), 1.96 (s, 3H), 2.54 (s, 3H), 4.82 (M 2H), 4.97 (d, J = 18.0, H) 5.17 (d, J = 9.0 Hz, H), 5.31 (d, J = 11.0, H), 5.80 (d, 17.5, H), 5.89−5.93 (m, H); 6.74 (dd, J = 18.0, 11.0, H), 7.13−7.16 (m, H), 7.27 (s, H), 7.28 (s, H), 7.40 (d, J = 2,

H), 7.4 (d, $J = 2.5$, H), 7.51 (s, H), 7.53 (d, $J = 2.0$, H), 7.60 (s, H), 7.62 (s, H), 7.71 (s, H). ^{13}C NMR (500 MHz, $CDCl_3$, TMS): δ 11.0, 22.8, 27.3, 46.3, 109.5, 114.9, 117.1, 119.6, 119.7, 121.5, 123.8, 126.7, 127.7, 132.3, 132.8, 136.0, 137.9, 154.3, 167.5, 168.3. HRMS (CI) *m*/*z* calcd for $C_{28}H_{26}N_2O_2$: 422.1994 (M^+). Found: 422.1983. Anal. Calcd for $C_{28}H_{26}N_2O_2$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.49; H, 6.26; N, 5.69.

2-[3-Methyl-1-(4-vinylbenzyl)-2-indolylmethene]-3-isopropylidene-*N*-(4-vinylphenyl)succinimide (**6**). The same setup as above; to a solution of fulgide **2** (0.252 g, 0.63 mmol) in benzene (12 mL), 4-vinylaniline (90%, 0.09 mL, 0.63 mmol) in benzene (5 mL) was added dropwise, and the reaction mixture was stirred for 1 h at room temperature. To this reaction mixture, zinc bromide powder (0.143 g, 0.63 mmol) was added in one portion. Subsequently, the reaction mixture was heated to refluxing temperature (80 °C), followed by the addition of hexamethyldisilazane (0.21 mL, 1.0 mmol) in benzene (5 mL) over a period of 10 min. This reaction mixture was then refluxed for 19 h. The crude product was purified by means of a flash silica gel chromatography column (chloroform as eluent) to afford a bright yellow crystal **6** (0.137 g, 43%). **6**: mp 149.5−150.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.17 (s, 3H), 1.96 (s, 3H), 2.50 (s, 3H), 5.21 (d, $J = 10.9$, H), 5.31 (d, $J = 10.9$, H), 5.37 (d, $J = 16.8$,H), 5.44 (s, $J = 16.8$, H), 5.68 (d, $J = 17.6$, H), 5.79 (d, $J = 17.6$, H), 6.63 (dd, $J = 17.6$, 10.9, H), 6.74 (dd, $J = 17.6$, 10.9, H), 7.01 (s, H), 7.03 (s, H), 7.17 (dd, $J = 7.7$, 7.1, H), 7.27 (s, H), 7.28 (s, H), 7.38 (s, H), 7.39 (s, H), 7.51 (s, H), 7.53 (s, H), 7.64 (dd, $J = 7.9$, H), 7.71 (s, H). ^{13}C NMR (500 MHz, $CDCl_3$, TMS): δ 11.1, 22.8, 27.2, 47.3, 109.6, 114.1, 114.9, 119.9, 124.0, 126.5, 126.7, 126.7, 126.8, 136.0, 136.2, 136.8, 137.4, 154.5, 167.5, 168.3. HRMS (CI) *m*/*z* calcd for $C_{34}H_{30}N_2O_2$: 498.2307 (M^+). Found: 498.2317. Anal. Calcd for $C_{34}H_{30}N_2O_2$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.73; H, 6.04; N, 5.60.

1-Allyl-3-methylindole (**8**). A 250 mL flask was charged with potassium hydroxide (41.6 g) in 150 mL of DMSO. The suspension was stirred at room temperature for 5 min, and 3-methylindole (20.9 g, 160 mmol) was added and subsequently stirred for 45 min. The flask was cooled in an ice−water bath, and the ally bromide (38.8 g, 320 mmol) was added dropwise. The mixture was stirred at room temperature for 1 h and subsequently poured onto 300 g of crashed ice. The product was extracted with three 150 mL portions of ethyl ether. The organic layers were combined, and the solvent was evaporated by rotary evaporation. The residue was purified by column chromatography on silica gel to give the product as a colorless oil (26.3 g, 96%) (hexane as eluent).

3-Methyl-1-(4-vinylbenzyl)indole (**9**). To a suspension of potassium hydroxide (10.2 g) in 80 mL of DMSO, 3-methylindole (5.24 g, 80 mmol) was added and subsequently stirred for 45 min at room temperature. The flask is cooled in an ice−water bath, and 4-vinylbenzyl chloride (90%, 6.6 g, 40 mmol) was added dropwise. The mixture was stirred at room temperature for 1.5 h and subsequently poured onto 100 g of crashed ice. After standing for 24 h, followed by filtration, the solid was collected. A white solid was afforded (7.75 g, 78.4%) after column chromatography on silica gel (hexane as eluent). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.33 (s, 3H), 5.22 (d, $J = 10.8$ Hz, H), 5.24 (s, 2H), 5.70 (d, $J = 17.6$ Hz, H), 6.66 (dd, $J = 17.6$, 10.8 Hz, H), 6.88 (s, H), 7.06−7.60 (m, 8H).

1-Allyl-3-methylindole-2-carboxaldehyde (**10**). A 250 mL, three-neck flask was charged with DMF (25 mL). At 0 °C, phosphoryl chloride ($POCl_3$, 9.0 g, 58.7 mmol) was added dropwise and stirred for 0.5 h under stirring. Subsequently, through a dropping funnel, **8** (8.6 g, 50.3 mmol) in DMF (5 mL) was added dropwise over a period of 20 min. After the addition was complete, the reaction mixture was stirred for 5 h at room temperature. To the resulting mixture, crushed ice (100 g) was added, followed by the careful addition of 10% aqueous sodium hydroxide until all of the acid was neutralized. The product was extracted with four 100 mL portions of ethyl acetate. The organic layers were combined, and the solvent was evaporated by rotary evaporation. The product was purified by column chromatography on silica gel (hexane−chloroform as eluent) and recrystallization from hexane. A white solid was obtained (8.2 g, 82%). **10**: mp 31−32 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.66 (s, 3H), 4.90 (dd, $J = 17.1$, 1.3 Hz, H), 5.09 (dd, $J = 10.3$, 1.3), 5.19 (d, 2H), 5.94−6.01 (m, H), 7.12−7.72 (m, 4H), 10.16 (s, H).

3-Methyl-1-(4-vinyl-benzyl)indole-2-carboxaldehyde (**11**). At 0 °C, phosphoryl chloride ($POCl_3$, 3 mL) was added dropwise to DMF (10 mL) and stirred for 0.5 h under stirring. Subsequently, **9** (6.0 g, 24.3 mmol) in DMF (3 mL) was added dropwise over a period of 20 min. After the addition was complete, the reaction mixture was stirred for 3 h at room temperature. To the resulting mixture, crushed ice (100 g) was added, followed by the careful addition of 10% aqueous sodium hydroxide until all the acid was neutralized. The product was extracted with four 100 mL portions of ethyl acetate. The organic layers were combined, and the solvent was evaporated. The product was purified by column chromatography on silica gel (hexane−chloroform as eluent) and recrystallization from hexane. A white solid was obtained (2.8 g, 42%). **11**: mp 85.5−86.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.66 (s, 3H), 5.18 (d, $J = 10.9$ Hz, H), 5.66 (d, $J = 17.6$ Hz, H), 5.77 (s, 2H), 6.63 (dd, $J = 17.6$, 10.9 Hz, H), 7.02 (s, H), 7.04 (s, H), 7.16−7.38 (m, 5H), 7.72 (d, $J = 8.1$ Hz, H), 10.16 (s, H).

Conclusion

New photochromic fluorescing copolymers have been synthesized by attaching fulgide or fulgimide chromophores to polymer chains forming novel copolymers of PMMA. We have shown that these copolymers have several important advantages over those photochromes dispersed in polymer matrices. The electronic absorption and fluorescence spectra and photochromic properties of the 2-indolyl fulgides and fulgimides copolymers have also been studied. We confirmed that the photochromic and spectroscopic properties of the copolymer remained the same as in solution.

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